PART I: SOLUBILITY OF DONOR SOLUTES IN HALOGENATED HYDROCARBONS

PART II: DISSOCIATION OF SUBSTITUTED HEXAARYLETHANES

BY

FREDERICK CURT DIETZ

A.B., Leland Stanford University, 1932

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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I. SOLUBILITY OF DONOR SOLUTES IN HALOGENATED HYDROCARBONS

INTRODUCTION

The concept of hydrogen bonding has recently [1] been extended to include bonding between a donor atom and hydrogen when it is attached to carbon. Considerable data has been obtained [2] to show that donor solvents such as esters, ethers, nitriles, and tertiary amines will dissolve certain hydrogen-containing halogenated hydrocarbons in excess of the amount calculated by Raoult's law. Completely halogenated methanes, on the other hand, could not form a hydrogen bond and no enhanced solubility was observed with these solutes.

Since donor solvents showed the ability to dissolve hydrogen bonding solutes in excess of the amounts calculated by Raoult's law it seemed logical that hydrogen-containing halogenated hydrocarbons would dissolve donor solutes in excess of the amounts calculated by Raoult's law. After making a literature survey of the solubility of organic compounds in chloroform and carbon tetrachloride the measurement of the solubility of eight polymeric solutes in both partially and completely halogenated hydrocarbons was undertaken.

DISCUSSION OF RESULTS

The solubilities of ninety-six organic compounds in both chloroform and carbon tetrachloride have been tabulated according to the ratio of their solubility in chloroform to their solubility in carbon tetrachloride. In only one case was this ratio less than unity. This seemed to indicate that chloroform is almost always a better solvent than carbon tetrachloride. In most cases in which the solubility ratio was greater than five it was possible to show that the formation of a solute solvent hydrogen bond would be expected. Most of the compounds that showed a solubility ratio less than five were not capable of acting as donor molecules for the hydrogen of chloroform, since they either had no donor centers or had associated with other solute molecules. Hydrocarbons, acids, and alcohols were the most predominate classes of compounds found in this group.

The solubilities of eight polymers in five different solvents were measured. Three of the solvents (chloroform, trichloroethylene, and tetrachloroethane) were capable of forming hydrogen bonds

with donor solutes while the other two (carbon tetrachloride and tetrachloroethylene) were not. Polymers with donor centers such as ethylene phthalate, superpolyhexamethylene adipate, superpolyethylene adipate, poly methyl methacrylate, polyvinyl acetate and poly methyl vinyl ketone showed a very much higher solubility in those solvents capable of hydrogen bonding than in solvents incapable of hydrogen bonding. Cellulose acetate, though theoretically containing many donor centers, did not exhibit quite the high solubility that was expected. The solubility of polyvinyl chloride was very low in all solvents. This result was expected since this polymer has no donor centers.

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II. DISSOCIATION OF SUBSTITUTED HEXAARYLETHANES

INTRODUCTION

Recent work[1] in this laboratory has shown that three factors in the dissociation of alkyl substituted hexaphenyl ethanes are apparently of considerable importance. One may be considered to be steric in nature, which is of primary importance when the substituent is in the *ortho* position. The second factor seems to be the symmetry of the ethane. The weight of the substituent has also been demonstrated[2] to be of importance, although its effect is often overshadowed by the other two.

In order to obtain additional data on the factors which may affect the dissociation of hexaphenylethanes this study of the halogen-substituted hexaphenylethanes was undertaken.

DISCUSSION OF RESULTS

The following halogen-substituted hexaphenylethanes have been prepared by well known procedures[3] and their degrees of dissociation measured by the magnetic susceptibility method:[4,5] di-*o*-fluorophenyltetraphenylethane (8 ± 1%), di-*o*-chlorophenyltetra-

phenylethane (12 ± 1%), di-*o*-bromophenyltetraphenylethane (17 ± 1%), di-*m*-chlorophenyltetraphenylethane (6.5 ± 1%), di-*m*-bromophenyltetraphenylethane (7 ± 1%), di-*p*-fluorophenyltetraphenylethane (3.5 ± 1%), di-*p*-chlorophenyltetraphenylethane (5 ± 1%), di-*p*-bromophenyltetraphenylethane (5 ± 1%), di-*p*-iodophenyltetraphenylethane (6 ± 1%), tetra-*p*-bromophenyldiphenylethane (7 ± 1%), hexa-*p*-chlorophenylethane (12 ± 2%), tetra-*p*-bromophenyldi-*p*-chlorophenylethane (2.5 ± 1%). All these measurements were made at 0.1 molar concentration in benzene solution at 25° C.

It has been shown that halogen-substituents increase the dissociation of hexaphenylethanes. In this series the effect is not as marked as in the alkyl-substituted hexaphenylethanes.[1] As the halogen substituent was changed to a less electronegative, heavier halogen an increase in the dissociation was always observed.

Steric factors have been shown to be important in *ortho*-substituted triarylmethyl radicals. *meta*-Substituents increase the dissociation more than *para*-substituents. The possibility of a factor which is operative in reducing the dissociation of halogen substituted radicals as compared with alkyl substituted radicals of same size and weight must be considered.

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[4] Roy, Ph.D. Thesis, University of Illinois.
[5] These measurements were made by Mr. C. M. Himel.

VITA

The writer was born in San Francisco, California, on April 20, 1911. He attended grammar and high school in Oakland, California. He entered Leland Stanford Junior University in the fall of 1928 and was granted the A.B. degree from that institution in the fall of 1932. From December, 1932, to August, 1933, he worked in the Refinery Technology Division of the Gulf Oil Company as a research chemist. The academic year 1933-1934 was spent in the Graduate School at Harvard University. From August, 1934, to August, 1936, the writer was employed as a chemist by the duPont Company at their plant at Deepwater, New Jersey. From September, 1936, to November, 1937, he was employed as a salesman by by the Dietz Motor Company, Alameda, California. In January, 1938, he entered the Graduate School of the University of Illinois and has continued in attendance at this school.

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